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Synergistic Rhodium/Copper Catalysis: Synthesis of 1,3-Enynes and *N*-Aryl Enaminones

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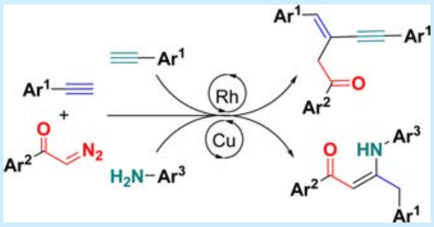
Supporting Information

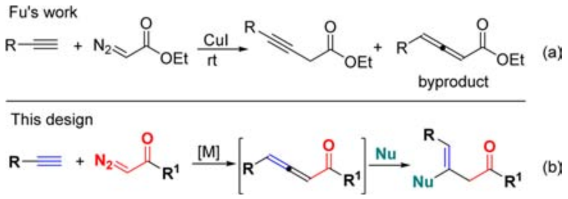
ABSTRACT: Synergistic rhodium/copper catalysis enables new three-component coupling reactions of terminal alkynes and α-diazoketones and/or arylamines, allowing dediazotized carbene C−H insertion for the synthesis of functionalized 1,3-enynes and *N*-aryl enaminones with high stereoselectivity. The synthetic utility of these transformations results in subsequent C−C or/and C−N bond-forming reactions to effectively build up functional molecules with potential significance.



1,3-Enynes are ubiquitous structural motifs found in a multitude of naturally occurring compounds and molecules of pharmaceutical and material interest.[1] For instance, with a 1,3-enyne subunit, terbinafine serves as a potent antimycotic agent for the treatment of skin mycoses.[2] Apart from their bioactive nature, 1,3-enynes are types of competent reactants endowed with multiple reactive sites, which could be used as versatile and synthetically useful building blocks[3] for the synthesis of functional molecules, including conjugated alkenes,[4] naphthalenes,[5] heterocycles,[6] and others,[7] because of their accessibility and broad functionalization potential for the flexible introduction of functional groups via addition across the π-C═C or C≡C bond system. To date, tremendous efforts have been devoted to developing efficient methodologies for 1,3-enyne syntheses, which has made it more applicable.[8] Generally, the vast majority of well-established protocols to access 1,3-enynes include metal-catalyzed Sonogashira coupling of terminal alkynes with vinyl halides,[9] dimerization of terminal alkynes,[10] Pd-catalyzed coupling between organometallic alkyne with alkene,[11] and Suzuki coupling of alkynyl halides with boronic acid,[12] the alkynylation of alkenylmetals,[13] and other methods.[14] Despite these significant advances, to the best of our knowledge, the utilization of a synergistic bimetallic strategy combined with a three-component reaction involved dediazotized carbene C−H insertion for the creation of functionalized 1,3-enynes has not yet been documented.

Diazo compounds are privileged synthons that have been extensively utilized for substantially challenging and intriguing syntheses over the years due to their high energy and diverse reactivity.[15] Fu and co-workers reported Cu-catalyzed coupling reaction of alkynes with ethyl diazoacetate (EDA) to produce 3-alkynoates, accompanied by a small quantity of the allene isomer (Scheme 1a).[16] As part of our continuing interest in the design of new metal-catalyzed coupling reactions[17] and considering the strong inductive effect of the keto-carbonyl group, we reasoned that under suitable conditions the use of α-diazoketones as replacements for EDA in the presence of metal catalysts could preferentially generate in situ allenyl ketones,[18] intercepted by nucleophiles (Nu) to yield functionalized β-alkenyl ketones with powerful potential applications (Scheme 1b). Here, we report the successful realization of this concept with a new and practical synergistic rhodium/copper catalysis in which a wide range of 1,3-enynes having a keto-carbonyl group were achieved through three-component reaction of α-diazoketones and terminal alkynes in 1:2 mole ratio (Scheme 2). This reaction pathway enables double C−C bond formation via dediazotized carbene C−H insertion under mild conditions using terminal alkynes as both a C−H insertion precursor and a nucleophilic component. Using arylamines as a nucleophile to expand the synthetic utility of this method, the reaction proceeds through a similar synergistic rhodium/copper catalysis, transforming into a series of important *N*-aryl enaminones with good yields and high stereoselectivity (up to 99:1 *Z*/*E*) (Scheme 2).

Scheme 1. Metal-Catalyzed Coupling of Alkynes with α-Diazocarbonyls



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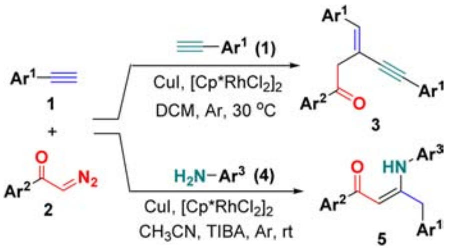
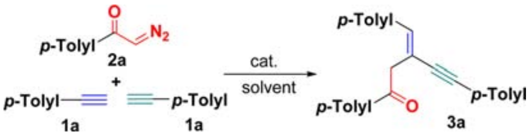
Scheme 2. Synthesis of 1,3-Enynes and *N*-Aryl Enaminones



The initial experiments were performed with 3.0 equiv of 4-ethynyltoluene (**1a**, excess) and 1.0 equiv of α-diazoketones **2a** in dry $CHCl_3$ at room temperature under a nitrogen atmosphere using $[Cp^*RhCl_2]_2$ (1 mol %) and CuI (10 mol %) as co-catalysts (Table 1). This set of conditions led to the expected 1,3-enyne product **3a**, albeit with a low 20% yield. Encouraged by this preliminary result, we next further optimized the reaction conditions. The effect of the solvent was first investigated (compare entries 2−6). The use of 1,2-dichloroethane (DCE) gave 1,3-enynes **3a** with a slightly higher yield (entry 2). Dichloromethane (DCM) facilitated this reaction process, delivering a 30% chemical yield of **3a**. Other solvents such as EtOH, 1,4-dioxane, and CH_3CN were proven ineffective for this transformation. Exchanging $[Cp^*RhCl_2]_2$ for $Rh_2(OAc)_4$ (1 mol %) also gave an inferior outcome by the use of DCM solvent (entry 7). Afterward, we attempted to employ other copper catalysts generally used in coupling reactions, such as CuBr and CuCl, to improve the reaction efficiency, but both showed inferior catalytic activities under standard conditions and gave relatively poor yields (entries 8 and 9). Without CuI, a much lower yield (13%) was obtained (entry 10), whereas the transformation does not proceed in the absence of $[Cp^*RhCl_2]_2$ (entry 11). Lowering the loading of CuI (5 mol %) decreased the yield of **3a**, but an increased yield was isolated as 2 mol % of $[Cp^*RhCl_2]_2$ was utilized (entries 12 and 13). Taking the combination of CuI (10 mol %) with $[Cp^*RhCl_2]_2$ (2 mol %), we varied other parameters including reaction temperature, additives, and component ratio. Elevating the temperature slightly to 30 °C proved more efficient, affording the expected 1,3-enynes **3a** in 48% yield. The use of additives like PivOH, AcOH, $FeCl_3$, $InCl_3$, and K_2CO_3 is harmful to the yields (see the Supporting Information). Gratifyingly, the reaction of **1a** and **2a** in a 5:1 mole ratio worked more efficiently, giving access to the desired 1,3-enynes **3a** in a 62% yield (entry 15).

Table 1. Optimization Conditions for Forming 3a[a]

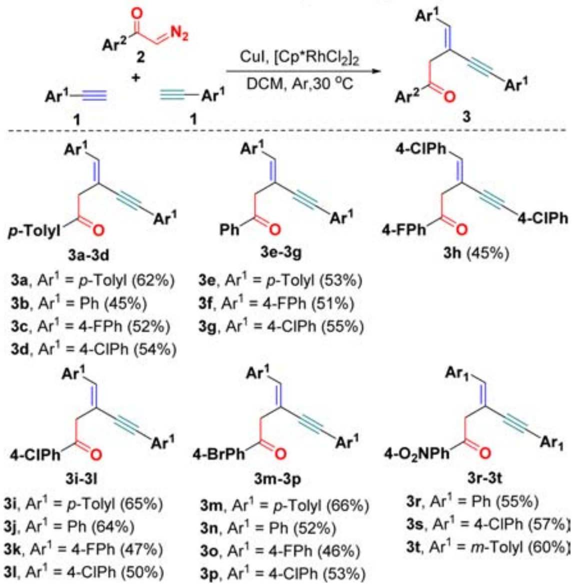


entry	cat. (mol %)	solvent	temp (°C)	yield[b] (%)
1	CuI (10)/RhL_n (1)	$CHCl_3$	rt	20
2	CuI (10)/RhL_n (1)	DCE	rt	22
3	CuI (10)/RhL_n (1)	DCM	rt	30
4	CuI (10)/RhL_n (1)	EtOH	rt	8
5	CuI (10)/RhL_n (1)	1,4-dioxane	rt	trace
6	CuI (10)/RhL_n (1)	CH_3CN	rt	trace
7	CuI (10)/$Rh_2(OAc)_4$ (1)	DCM	rt	18
8	CuBr (10)/RhL_n (1)	DCM	rt	trace
9	CuCl (10)/RhL_n (1)	DCM	rt	15
10	RhL_n (1)	DCM	rt	13
11	CuI (10)	DCM	rt	ND
12	CuI (5)/RhL_n (1)	DCM	rt	25
13	CuI (10)/RhL_n (2)	DCM	rt	35
14	CuI (10)/RhL_n (2)	DCM	30	48
15	CuI (10)/RhL_n (2)	DCM	30	62[c]

[a] Reaction conditions: 4-ethynyltoluene (**1a**, 1.5 mmol) and α-diazoketones **2a** (0.5 mmol), dry solvent (3.0 mL), RhL_n = $[Cp^*RhCl_2]_2$, under argon conditions, room temperature, 14 h. [b] Isolated yield based on **2a**. [c] The mole ratio of **1a** and **2a** in 5:1. ND = not detected.

With the optimization of reaction conditions in hand, the generality of this bimetallic Rh/Cu co-catalyzed coupling of terminal alkynes with α-diazoketones was investigated carefully. As shown in Scheme 3, α-diazoketone **2a** was first subjected to reaction of terminal alkynes with different electronic properties, and the expected 1,3-enynes **3a−d** were obtained in synthetically useful yields. Various terminal arylalkynes having substituents at the *para*-position with electron-rich (methyl, **1a**), electron-neutral (H, **1b**), and electron-poor (fluoro, **1c**; chloro, **1d**) groups were compatible. Next, the scope of the α-diazoketones **2** was explored by the adoption of these four examples of representative terminal arylalkynes as the coupling partner. As we had expected, these reactions proceeded smoothly to give access to the corresponding 1,3-enyne products. For instance, the use of α-diazoketone **2b** with an electron-neutral substituent led to the desired 1,3-enynes **3e−g** in 51%−55% yields. Similarly, functional groups like fluoro (**2c**), chloro (**2d**), and bromo (**2e**) at the *para*-position of substrates **2** can tolerate the bimetallic catalytic conditions well. Alternatively, α-diazoketones carrying a strong electron-withdrawing group (NO_2) still showed high reactivity in current synergistic rhodium/copper catalysis, generating the corresponding products **3r−t** with yields ranging from 55% to 60%.

Scheme 3. Substrate Scope for Synthesis of 3[a]



[a] Yields of isolated products based on substrate **2** after column chromatography on silica gel are given. **1** (0.5 mmol) and **2** (2.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), CuI (10 mol %), dry DCM (3.0 mL), Ar, 14 h.

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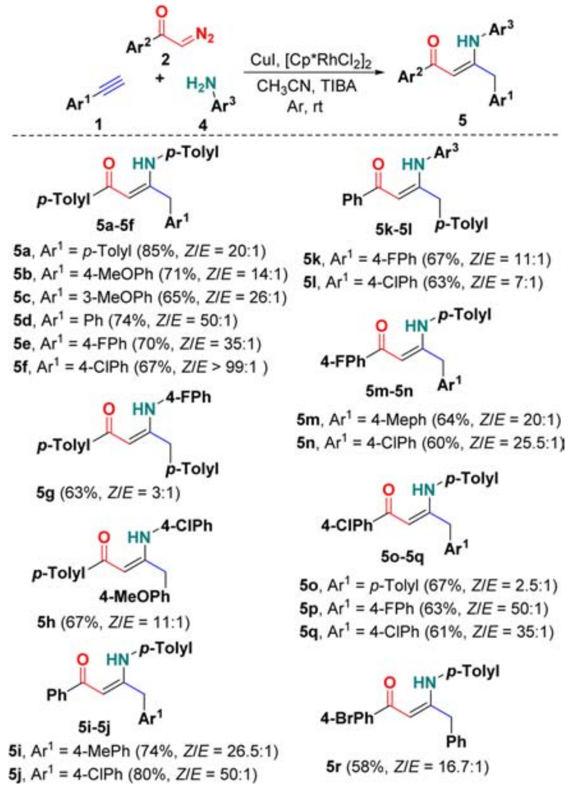
After the successful formation of 1,3-enynes **3**, we turned our attention to evaluating the feasibility of the construction of *N*-aryl enaminones by replacement of one molecule of terminal arylalkynes with arylamines as a nucleophilic component. The reaction of **1a** with **2a** and arylamines **4a** was conducted under the above-described conditions, but only 20% yield of *N*-aryl enaminones **5a** was obtained (see the Supporting Information, Table S2, entry S1). Next, both bases and solvents were adjusted to search for the optimized conditions (Table S2). The use of 2.0 equiv of inorganic bases such as K_2CO_3 and Cs_2CO_3 in DCM was met with little success (entries S2 and S3), whereas a slight improvement was observed when triethylamine (Et_3N, 2.0 equiv) was used as an organic base (entry S4). Increasing the amount of Et_3N led to a slightly higher yield (38%, entry S5). Switching the solvent from DCM to acetonitrile in the presence of Et_3N furnished **5a** in a 43% isolated yield (entry S6). Other solvents such as 1,4-dioxane, DCE, toluene, and $CHCl_3$ were inferior to acetonitrile in terms of reaction yields (entries S7−S10). No significant improvement of the coupling yield was achieved as tripropylamine (TPA) was served as a base promoter (entry S11). Interestingly, both tributylamine (TBA) and triisobutylamine (TIBA) facilitated this transformation to improve the reaction efficiency (entries S12 and S13), and TIBA gave a best outcome (74%). After careful optimization, we found that fine-tuning of the component mole ratio to 1.5:1.5:1 in the presence of TIBA afforded the expected *N*-aryl enaminones **5a** in an 85% yield (entry S14).

With the established optimal conditions, we then set out to evaluate the scope and limitation of our domino strategy by treating a variety of terminal alkynes with a range of α-diazoketones and arylamines (Scheme 4). Upon repeating the reaction with α-diazoketones **2a** and arylamines **4a**, we were pleased to find that terminal arylalkynes **1** bearing electron-donating, -neutral, and -withdrawing substituents at the *para*- or *meta*-positions of the phenyl ring participated well in this synergistic bimetallic catalysis, delivering the collection of highly substituted *N*-aryl enaminones (**5a**−**f**) in good to excellent yields of 65−85% with the *Z*/*E* ratio between >99/1 and 14/1. We believe this high stereoselectivity depends on intramolecular hydrogen-bond formation.[19] The influence of substituted α-diazoketones and aromatic amines was next explored, employing arylalkynes **1** with different functionalities on the aromatic ring including methyl, methoxy, fuloro, and chloro groups. The results indicated that both electron-rich and electron-poor counterparts are suitable substrates, giving access to the corresponding *N*-aryl enaminones **5g**−**r** in overall acceptable yields (up to 80%) with generally high stereoselectivity (except **5g**, **5l**, and **5o**) through a dediazotized carbene C−H insertion process. Note that this is the first reported procedure for the three-component assembly of these new functionalized 1,3-enynes and *N*-aryl enaminones through a sequential Rh-/Cu-catalyzed carbene C−H insertion/nucleophilic addition pathway in a one-pot manner. Single-crystal X-ray diffraction analysis of **3i** and **5a** was conducted for further structural confirmation.

On the basis of the above observations and report survey,[20] a reasonable mechanism for the formation of products **3** and **5** is proposed (see the Supporting Information, Scheme S1). In the presence of rhodium catalyst, α-diazoketones are converted into rhodium carbenoid **A**, which undergoes ligand exchange and migration insertion to afford oxa-π-allyl Rh intermediate **C**,[21] followed by enolization[22] to intermediate **D**. Compound **D** is transformed into allene intermediate **E** and regenerates rhodium catalyst. Nucleophilic addition of nucleophile (Nu) into allene intermediate **E** gives final products **3** and **5**.

Scheme 4. Substrate Scope for Synthesis of 5[a]



[a]Yields of isolated products based on substrate **4** after column chromatography on silica gel are given. Conditions: **1** (0.75 mmol), **2** (0.75 mmol), and **4** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), CuI (10 mol %), TIBA (2.0 mmol), dry CH_3CN (5.0 mL), Ar, 12 h.

In conclusion, we have established a new synergistic bimetallic-catalyzed three-component coupling of terminal alkynes and α-diazoketones and/or arylamines, by which a wide range of functionalized 1,3-enynes and *N*-aryl enaminones can be synthesized through dediazotized carbene C−H insertion. The former enables double C−C bond formation through synergistic rhodium/copper catalysis, allowing us to build blocks of 1,3-enynes having a keto-carbonyl group with a wide diversity in substituents. In the latter, a range of *N*-aryl enaminones with flexible structural modification was accomplished in a highly stereoselective manner. The experimental results indicated that the reaction might be initiated by the in situ formation of rhodium carbenoid followed by a migratory insertion/nucleophilic addition sequence. A detailed application of the resulting 1,3-enynes and *N*-aryl enaminones is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00238.

Experimental procedures and spectroscopic data for all new compounds **3a**−**t** and **5a**−**r** (PDF)

X-ray crystal data for **3i** (CIF)

X-ray crystal data for **5a** (CIF)

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Notes

The authors declare no competing financial interest.

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